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ARTICLES

Deduction of the Activation Parameters for Ring Expansion and Intersystem Crossing in Fluorinated Singlet Phenylnitrenes

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The ratio $(k_{exp} + k_{isc})/k_{PYR}$ was determined as a function of temperature for the singlet nitrenes derived from pentafluoro, 2,6-difluoro, and 2,4,6-trifluorophenyl azide where k_{PYR}, k_{exp}, and k_{isc} are the absolute rate constants of reaction of the nitrene with pyridine, ring expansion, and intersystem crossing, respectively. Activation parameters were deduced for the three singlet nitrene processes.

I. Introduction

The complex photochemistry of aryl azides[1] and their utility in photoaffinity labeling experiments have been extensively discussed.[2] It is clear that photolysis of phenyl azide (**1,0**) (Scheme I) and its simple derivatives releases singlet arylnitrenes. Singlet phenylnitrene (**2,0,S**) cannot be intercepted by external trapping reagents. At ambient temperatures singlet phenylnitrene ring expands rapidly to ketenimine **3,0**, which is the only trappable intermediate produced on photolysis of phenyl azide at ambient temperature.

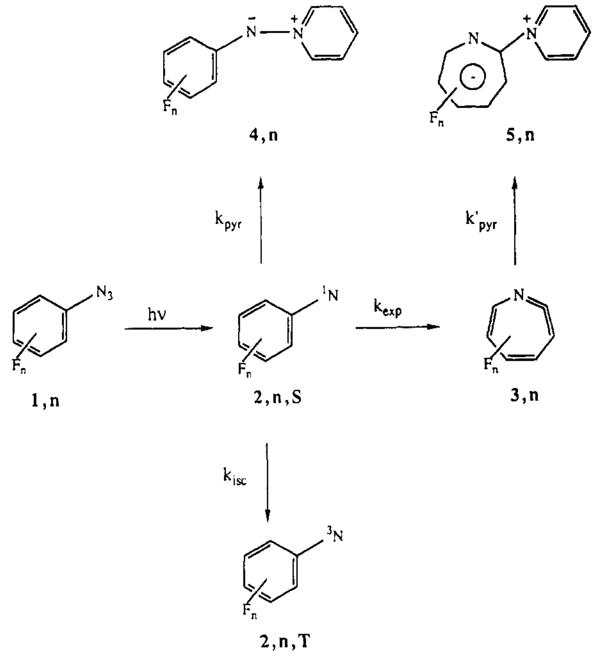
At lower temperatures the ring expansion process is retarded because it has a significant activation barrier, and intersystem crossing (ISC) to triplet phenylnitrene (**2,0,T**) begins to play a significant role as a competitive process.[3] The temperature-dependent photochemistry of phenyl azide in the presence of diethylamine indicates that singlet phenylnitrene (**2,0,S**) is the branching point in this process. A differential activation barrier to ring expansion and intersystem crossing of 3 ± 1 kcal/mol was deduced (Scheme I) for singlet phenylnitrene.

Fluorination has a dramatic effect on the photochemistry of phenyl azide,[4] and fluorinated singlet arylnitrenes can be trapped by pyridine and diethylamine to give adducts in respectable yields. It was recently shown that fluorination at both the ortho and ortho′ positions (2,6-difluoro-(**1,2**), 2,4,6-trifluoro-(**1,3**), and pentafluorophenyl azides (**1,5**) or less effectively fluorination in the ortho and para positions (2,4-difluorophenyl azide) is required to trap the corresponding singlet nitrene.[4-8]

In the absence of any quencher, the major product of photolysis of fluorinated aryl azides at ambient temperature is again ketenimine **3,n**. Fluorination results in a more favorable ratio of k_{pyr}[pyr] to k_{exp} by retarding the rate of ring expansion of the singlet nitrene. This retardation in the rate of ring expansion results in a significant shift in the isokinetic temperature, the temperature at which the ISC rate equals the rate of the ring expansion process. The isokinetic temperature is about −165 °C for phenyl azide, but perfluorination raises this temperature to between −10 and −30 °C.[6]

In spite of the large interest in aryl azides and their fluorinated derivatives, the activation parameters for ring expansion and intersystem crossing are still unknown. In this paper we have deduced activation parameters for selected fluorinated phenyl azides using the pyridine ylide probe method.[11]

SCHEME I



n=0	1,0	phenyl azide
n=2	1,2	2,6-difluorophenyl azide
n=3	1,3	2,4,6-trifluorophenyl azide
n=5	1,5	pentafluorophenyl azide

II. Experimental Section

The experimental apparatus has been described elsewhere and will only be summarized here.[10]

Solutions of the azides were investigated in CH_2Cl_2 solution containing pyridine in quartz cuvettes and were photolyzed with the 308-nm laser line of a Lambda Physik XeCl excimer laser (17 ns, 150 mJ).

Solutions were degassed prior to photolysis by bubbling with argon for 5 min. Because of the large photochemical conversion of azide to product in each laser pulse, the samples were changed after every laser shot.

Temperature was controlled in a special cryostat with quartz windows by passing liquid coolant at the required temperature through a jacket around the sample. Fluctuation of the temperature was measured with a platinium thermoelement and did

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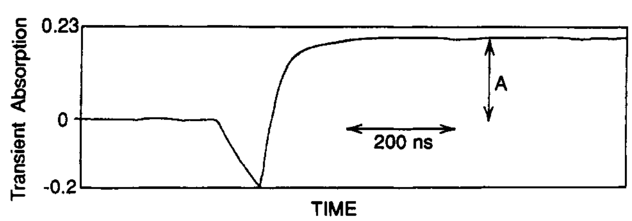

Figure 1. Growth of the transient absorption of nitrene pyridine ylide **4,n** following laser flash photolysis of pentafluorophenyl azide **1,5** in CH_2Cl_2 and [pyridine] = 0.05 M at ambient temperature.

not exceed 1 °C. Each sample was thermostated for 10 min prior to laser flash measurements.

Dichloromethane was dried by distillation over molecular sieves. Pyridine was purified by distillation over barium hydroxide and stored over KOH.

The synthesis of 2,6-difluoro-, 2,4,6-trifluoro-, and pentafluorophenyl azides used in this study has been described elsewhere.[4-8]

The concentration of the aryl azides was kept constant with an optical density at 308 nm of 0.7.

A 375-nm cutoff filter was placed between the Xenon arc monitoring lamp and the sample to minimize exposure of the sample to UV light.

III. Results

The reactive triplet nitrene and ketenimine intermediates produced on photolysis of aryl azides are well characterized by various spectroscopic methods.[11] However, singlet arylnitrenes have not yet been detected directly by any spectroscopic methods.

UV–vis spectroscopy reveals that there are four major bands of triplet phenylnitrene at about 240, 320, 400, and 500 nm which are a little shifted towards longer wavelengths upon ring fluorination.[3a] Triplet phenylnitrene is very sensitive to light, and even low-energy analyzing light leads to the rapid isomerization of triplet nitrene to ketenimine.

Ketenimine **3,0** absorbs in the UV region with a broad maximum in the region 340–360 nm.[12] In the absence of a nucleophilic quencher ketenimine **3,0** polymerizes, and the absorption at 340–360 nm increases at long times *after* flash photolysis due to formation of the polymer.

Because of the short lifetimes of the intermediates and overlapping of the absorption bands of products, it is impossible to directly determine the rate constants of ring expansion and nitrene formation by nanosecond spectroscopy.

However, it has been previously[4,5] demonstrated that both singlet nitrenes and ketenimines react with pyridine to form ylides. The pyridinium ylides have very intense absorption spectra and long lifetimes which make them ideal probes of transient phenomena.[4,5,9] Ylides derived from singlet nitrenes **4,n** (390–410 nm) and ketenimines **5,n** (500–520 nm) absorb in very different spectral regions, and their spectra do not vary substantially with fluorine substitution.

Those aryl azides which have fluorine atoms in both the ortho and ortho′ positions produce on photolysis singlet nitrene **2,n,S** whose reaction with pyridine is favored over ring expansion. In these cases ketenimine **3,n** may be trapped only in the presence of very low concentrations of pyridine. An increase in the concentration of pyridine leads to a decrease in the intensity of the absorption band of ketenimine ylide **5,n** with a corresponding increase in the absorption band of nitrene ylide **4,n**. At higher concentrations of pyridine, however, every singlet nitrene **2,n,S** produced in a laser pulse is captured by pyridine to form ylide **4,n**, and the nitrene ylide absorption reaches saturation.[5,13] Unfortunately, the growth of the transient absorption of the singlet nitrene pyridine ylide cannot be resolved by nanosecond spectroscopy, and only an optical yield (A) of ylide can be measured as a function of the concentration of pyridine (Figure 1). According to Scheme I, a double-reciprocal plot of $1/A$ vs $1/[\text{pyr}]$ should be linear with a ratio of slope/intercept equal to k_o/k_{pyr}:

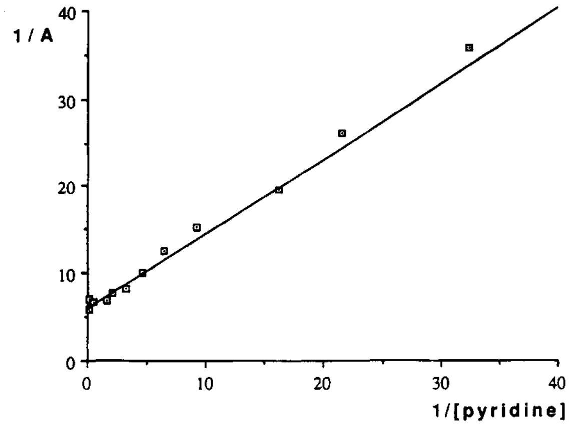

Figure 2. Double-reciprocal plot of $1/A$ vs 1/[pyridine] for the yield of nitrene pyridine ylide **4,n** obtained by LFP of pentafluorophenyl azide **1,5** at ambient temperature.

$$\frac{1}{A} = \frac{1}{A^{\text{SAT}}\phi_{\text{N}}}\frac{k_o}{k_{\text{pyr}}}\frac{1}{[\text{pyr}]} + \frac{1}{A^{\text{SAT}}\phi_{\text{N}}} \qquad (1)$$

where A^{SAT} is the optical density in the saturation region, k_{pyr} is the absolute rate constant of reaction of the singlet nitrene with pyridine, ϕ_{N} is the quantum yield of nitrene formation, and k_o is sum of all rate constants of all processes which consume the singlet nitrene in the absence of pyridine. According to Scheme I, and in the absence of any quenchers which can react with the singlet nitrene, these processes are limited to intersystem crossing (k_{isc}) and ring expansion to ketenimine (k_{exp}), and $k_o = k_{\text{isc}} + k_{\text{exp}}$.

The dependence of the optical yield of nitrene ylide on the concentration of pyridine upon laser flash photolysis (LFP) of the requisite azide is presented as a double-reciprocal plot with pentafluorophenyl azide in Figure 2.

Values of k_o/k_{pyr} were determined at seven different temperatures over a 40 to −50 °C temperature range for three fluorinated compounds: 2,6-difluoro-(**1,2**), 2,4,6-trifluoro-(**1,3**), and pentafluorophenyl azides (**1,5**). At temperatures above 50 °C, a dark reaction which consumes azide precursor makes additional measurements impossible.

For 2,4-difluorophenyl azide, ring expansion is exceptionally fast, and even in the presence of large concentrations of pyridine the broad and intense ketenimine ylide transient absorption is present in the spectrum. Because of partial overlapping with the nitrene ylide absorption, the results with this azide were not considered in the present calculations.

Arrhenius type plots of $\ln(k_o/k_{\text{pyr}})$ vs $1/T$ are presented in Figures 3–5.

Because $k_o = k_{\text{isc}} + k_{\text{exp}}$, the plots presented in Figures 3–5 can be expanded to give eq 2

$$\ln\{(k_{\text{isc}} + k_{\text{exp}})/k_{\text{pyr}}\} = \ln\{[A_{\text{isc}} + A_{\text{exp}} \exp(-E_{\text{exp}}/RT)]/A_{\text{pyr}} \exp(-E_{\text{pyr}}/RT)\} \qquad (2)$$

where A_{isc}, A_{exp}, and A_{pyr} are pre-exponential factors for intersystem crossing, ring expansion, and reaction with pyridine, respectively. The terms E_{exp} and E_{pyr} are the activation barrier for ring expansion and reaction with pyridine, respectively. We assume in eq 2 that intersystem crossing has zero activation energy as per singlet to triplet carbene intersystem crossing, which has little or no temperature dependence.[14]

It is difficult at best to obtain five unknown parameters from one experimental relation; however, the characteristic shape of these plots immediately leads us to a few conclusions. First, both ring expansion and the reaction of the singlet nitrene with pyridine must have a positive activation barrier, and the ring expansion

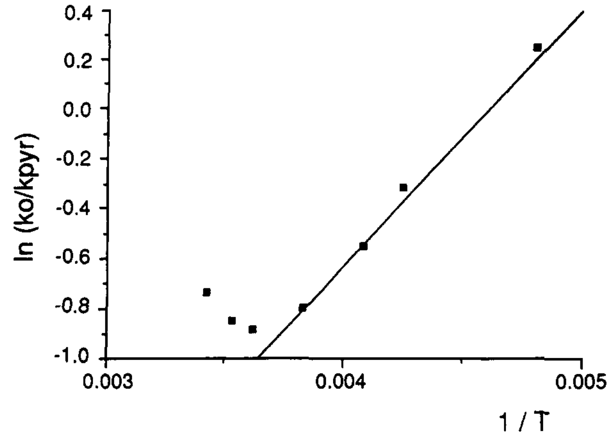

Figure 3. Arrhenius plot of $\ln(k_o/k_{pyr})$ vs $1/T$ obtained with 2,6-difluorophenyl azide **1,2**.

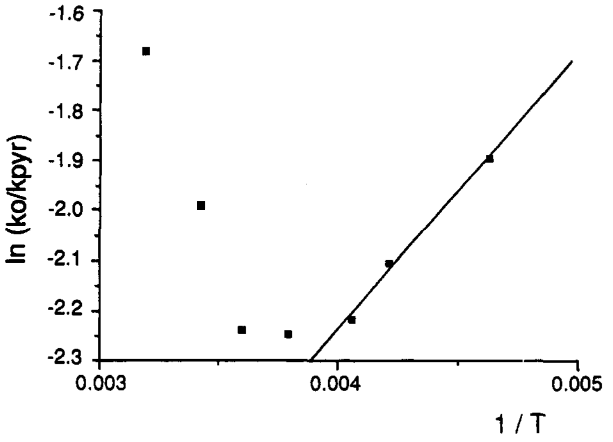

Figure 4. Arrhenius plot of $\ln(k_o/k_{pyr})$ vs $1/T$ obtained with 2,4,6-trifluorophenyl azide **1,3**.

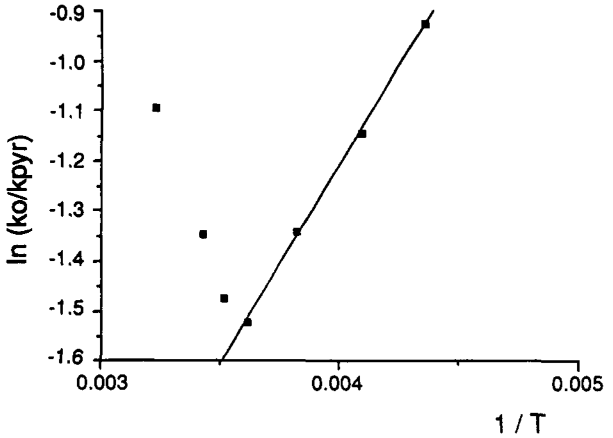

Figure 5. Arrhenius plot of $\ln(k_o/k_{pyr})$ vs $1/T$ obtained with pentafluorophenyl azide **1,5**.

process must have the larger barrier of the two processes. Additionally, the experimental plots show that all compounds have a minimum in their Arrhenius plots at almost the same temperature, T_{min} (about 0 °C). Thus we can obtain an additional relation by equating the derivative of eq 2, with respect to temperature, to zero. This leads to eq 3:

$$A_{exp}\exp(-E_{exp}/RT_{min}) = A_{isc}[E_{pyr}/(E_{exp} - E_{pyr})] \quad (3)$$

At low temperatures where product studies demonstrate that $k_{isc} \gg k_{exp}$, eq 2 simplifies to

$$\ln(A_{isc}/A_{pyr}) + E_{pyr}/RT = \ln(k_o/k_{pyr}) \quad (4)$$

TABLE I: Activation Parameters[a] Obtained by the Best Fit of the Experimental Results to Simulated Eq 2: $A_{exp} = 1 \times 10^{13}$ s^{-1}

	pentafluorophenyl azide **1,5**	2,4,6-trifluorophenyl azide **1,3**	2,6-difluorophenyl azide **1,2**
	A_{pyr} on the Order of 10^{10} s^{-1}		
E_{exp} (cal/mol)	7150	6950	7000
A_{isc}(s^{-1}) = k_{isc}	7.0×10^7	1.2×10^8	7.4×10^7
A_{pyr} (M^{-1} s^{-1})	6.3×10^9	1.1×10^{10}	1.15×10^{10}
E_{pyr} (cal/mol)	1100	1600	2150
k_{exp} (s^{-1})	6.2×10^7	8.6×10^7	7.9×10^7
k_{pyr} (M^{-1} s^{-1})	9.9×10^8	7.5×10^8	3.1×10^8
	A_{pyr} on the Order of 10^9 s^{-1}		
E_{exp} (cal/mol)	8500	8350	8400
A_{isc} (s^{-1}) = k_{isc}	8.5×10^6	1.2×10^7	7.5×10^6
A_{pyr} (M^{-1} s^{-1})	7.2×10^8	1.1×10^9	1.1×10^9
E_{pyr} (cal/mol)	1100	1600	2150
k_{exp} (s^{-1})	6.4×10^6	8.2×10^6	7.6×10^6
k_{pyr} (M^{-1} s^{-1})	1.1×10^8	7.5×10^7	3.0×10^7

[a] k_{exp}, k_{pyr} at 25 °C.

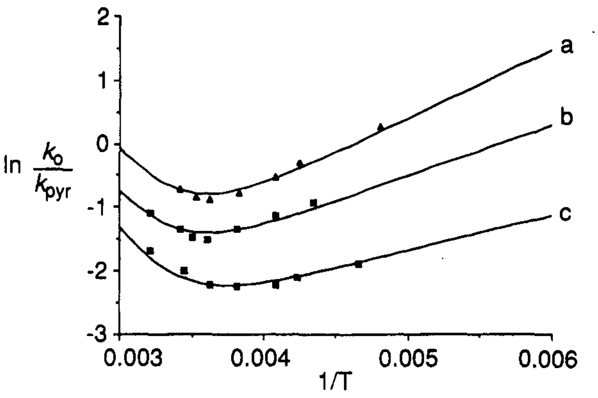

Figure 6. Equation 2 calculated from the activation parameters of Table I (solid lines) and compared to the experimental results obtained with (a) 2,6-difluorophenyl azide **1,2**, (b) 2,4,6-trifluorophenyl azide **1,3**, and (c) pentafluorophenyl azide **1,5**. $A_{pyr} = 10^9$ M^{-1} s^{-1}.

Analysis of the linear part of the experimental plots at low temperatures yields values of A_{isc}/A_{pyr} and E_{pyr}. Unfortunately, the high-temperature region of the Arrhenius plots is quite limited, preventing reliable analysis of the data.

Assuming that ring expansion to ketenimine has a normal Arrhenius pre-exponential factor ($A_{exp} = 10^{13}$ s^{-1}) for a unimolecular rearrangement, we simulated eq 2 with different values of the pre-exponential factor of the reaction of the singlet nitrene with pyridine (A_{pyr}).

Activation parameters presented in Table I were calculated by holding A_{pyr} constant at either 10^9 or 10^{10} s^{-1}. The fitting of the experimental data to simulated eq 2 is presented in Figure 6 for $A_{pyr} \sim 10^9$ s^{-1}. It is clearly seen that the calculated curve fits the experimental data quite well.

Fitting of the experimental data for $A_{pyr} = 10^{10}$ s^{-1} is only slightly worse than with $A_{pyr} = 10^9$ s^{-1}. Because of the experimental error, the calculated activation parameters obtained with values of A_{pyr} fixed between 10^7 and 10^9 s^{-1} cannot be immediately excluded (Figure 7). However, the magnitudes of all the rate constants obtained for $A_{pyr} < 10^9$ s^{-1} predict low values of k_o and that the growth of the singlet nitrene pyridine ylide should be resolved in our nanosecond laser flash photolysis experiment, but this is not the case (see Figure 1).

IV. Discussion

The magnitude of k_{pyr} has not been measured directly for the reaction of singlet arylnitrenes with pyridine. However, the rate constant of this reaction must be slower than that of a diffusion-controlled process (10^{10} M^{-1} s^{-1}). Because we cannot resolve the absolute rate of formation of nitrene ylide when [pyridine] = 0.5

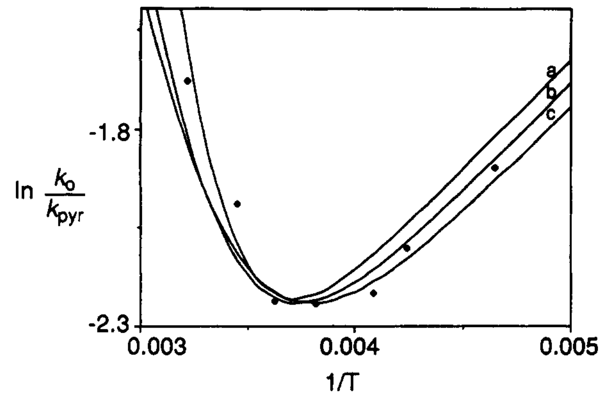

Figure 7. Fitting of eq 2 for pentafluorophenyl azide 1,5 data with (a) $A_{pyr} = 10^7$ M^{-1} s^{-1}, (b) $A_{pyr} = 10^9$ M^{-1} s^{-1}, and (c) $A_{pyr} = 10^{10}$ M^{-1} s^{-1}.

M, the magnitude of k_{pyr} must exceed 1×10^7 M^{-1} s^{-1}. A value of k_{pyr} commonly observed with carbenes is 10^9 M^{-1} s^{-1}.[11] The activation parameters ($A_{pyr} = 10^{9-10}$ M^{-1} s^{-1}) of Table I indicate that the value of k_{pyr} must vary between 3×10^7 and 1×10^9 M^{-1} s^{-1} at ambient temperature. We believe that $k_{pyr} \approx 3 \times 10^7$ M^{-1} s^{-1} because laser flash photolysis studies show that 4-azidotetrafluorobenzamides produce very long lived nitrenes.[15] In these cases, k_{pyr} can be measured absolutely and was found to be 3×10^7 M^{-1} s^{-1}. Thus, the entries of Table I which predict values of k_{pyr} closest to 3×10^7 M^{-1} s^{-1} are preferred at this time.

The differences observed in the activation barrier for the reaction with pyridine are not significantly different for the three fluorinated arylnitrenes of this study.

The rate constant of intersystem crossing of 10^{7-8} s^{-1} is faster than we have deduced earlier[6] but is still 10–100 times slower than that found with arylcarbenes where ISC is on the order of 10^9 s^{-1}. Because the rates of radiationless transitions are fastest when singlet and triplet states are very close in energy, the slow rate of arylnitrene ISC relative to that observed with carbenes may be a consequence of a much larger singlet–triplet energy gap in fluorinated arylnitrenes than is present in arylcarbenes (for example, the singlet–triplet splitting in NH is 35 kcal/mol compared to that of CH_2: 9.5 kcal/mol)[16] or difference s in the electron configurations of singlet arylcarbenes and arylnitrenes.[15]

The activation barrier of 7–8.5 kcal/mol for ring expansion is in good agreement with earlier predictions based on chemical studies[6] and is much higher than the barrier deduced for ring expansion of singlet phenylnitrene of 3 ± 1 kcal/mol.[3a]

The activation parameters for ring expansion do not vary between the three fluorinated aryl azides studied in this work. The results indicate that the 2,6 substitution pattern plays a key role in controlling the rate of ring expansion. We believe that the π^2 configuration of fluorinated singlet phenylnitrenes expands to form a ketenimine by sliding a pair of electrons into the adjacent empty σ orbital centered on nitrogen. This configuration may be less accessible in fluorinated compounds than in singlet phenylnitrene due to differential stabilization of the $^1(\sigma,\pi)$ and $^1(\sigma^2)$ configuration of the fluorinated arylnitrene. These configurations may well be stabilized both by π back-bonding of the nonbonding electrons of fluorine into an empty π orbital of the nitrene nitrogen and by stabilization of the filled, in-plane σ orbital on nitrogen by delocalization onto fluorine. Fluorine substitution may also destabilize ketenimines when positioned on the cumulene double bonds and thus retard ring expansion of the nitrene.

The difference in the activation barrier for ring expansion between fluorinated and parent singlet phenylnitrene is large enough to explain the observed shift in the isokinetic temperature of the rates of ring expansion and intersystem crossing if the rate constant of intersystem crossing for parent phenyl azide is the same order of magnitude as that deduced for the fluorinated compounds: 10^{7-8} s^{-1}.

Because fluorinated singlet arylnitrenes react with a wide range of substrates and with large rate constants, this is an especially important factor in photoaffinity labeling experiments. A change in the substitution pattern which leads to an increase of the lifetime of an arylnitrene will play a crucial role in the utility of these compounds. Fluorination of the aryl ring has a significant effect on the rate of ring expansion and thus on the lifetime of the singlet nitrene. However, it seems that retardation of ring expansion reaches a practical limit on extending the lifetime of singlet arylnitrenes because a further increase in the activation barrier for this process will not change the lifetime of nitrene due to the fact that ISC will begin to compete with ring expansion, even at ambient temperatures. Unless substitution does not retard ISC, the lifetime of the singlet nitrene can not be increased beyond the present values deduced in this study.

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